

543. *The Activation of Carbon-Carbon Double Bonds by Cationic Catalysts. Part II.* The Effect of para-Substituents and of Solvents on the Dimerization of Diarylethylenes.*

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The dimerization of 1:1-di-*p*-tolylethylene and of 1-*p*-anisyl-1-phenylethylene to the corresponding butene dimers, and the reverse reactions, were followed dilatometrically, trichloroacetic acid being used as catalyst, and benzene as solvent. For both these olefins, the rate-determining step in the forward direction is the attack of a monomer ion on a monomer molecule, and that in the reverse direction is the breakdown of the dimer ion. In this respect these olefins behave similarly to 1:1-diphenylethylene (see Part I).

The corresponding reaction for 1:1-di-*p*-methoxyphenylethylene has been followed in detail in the forward direction only: attempts to isolate the dimer gave only an oil. In contrast to the results obtained for the above monomers, the rate-determining step for the dimerization of 1:1-di-*p*-methoxyphenylethylene is the formation of the monomer ion.

Dimerization of 1:1-diphenylethylene with trichloroacetic acid as catalyst, and the reverse reaction have been examined in nitroethane. The rate-determining steps are the same as in benzene, but the order in acid for both the forward and the reverse reaction is 2.4, and not 3.0 as in benzene. We interpret this difference as due to the smaller participation of acid molecules in the solvation of the ionic intermediates in the more polar solvent.

A preliminary spectrophotometric study of the system benzene-trichloroacetic acid-1:1-di-*p*-methoxyphenylethylene gives some indication of the nature of the ionic intermediates occurring in such acid-catalysed olefin reactions.

IN Part I we reported the dimerization of 1:1-diphenylethylene in benzene when trichloroacetic acid is used as catalyst. This work has been extended to the similarly

* Part I, A. G. Evans, Jones, and Thomas, *J.*, 1955, 1824.

catalysed reactions of 1 : 1-di-*p*-tolylethylene, 1-*p*-methoxyphenyl-1-phenylethylene, and 1 : 1-di-*p*-methoxyphenylethylene in benzene and of 1 : 1-diphenylethylene in nitroethane.

EXPERIMENTAL

Materials.—Trichloroacetic acid, 1 : 1-diphenylethylene, and benzene were purified as outlined in Part I. 1 : 1-Di-*p*-tolylethyl alcohol was prepared by the action of *p*-tolylmagnesium bromide on 4-methylacetophenone. The alcohol was dehydrated by two distillations at reduced pressure, and the white 1 : 1-di-*p*-tolylethylene obtained was recrystallized from dry light petroleum (b. p. 40—60°), and had m. p. 62.5—63.0°, agreeing with that given in the literature.¹

1 : 1 : 3 : 3-Tetra-*p*-tolylbut-1-ene was obtained in a way similar to that used for the dimer of 1 : 1-diphenylethylene (see Part I), but the following more rigorous purification was adopted in the present work. The dimer was washed with glacial acetic acid, and then boiled with water to remove sulphuric acid. It was recrystallized from glacial acetic acid to remove monomer, and then from light petroleum (b. p. 60—80°). It was fused under a high vacuum, and recrystallized from dry light petroleum (b. p. 60—80°). A pure white powder was obtained of m. p. 107.5—108.0° (lit.,² m. p. 107.5—108.0°).

1-*p*-Methoxyphenyl-1-phenylethylene was prepared from the corresponding alcohol as described above, and the white solid recrystallized from light petroleum. The product had m. p. 75° (lit.,^{2,3} m. p. 75°). The alcohol was obtained by the action of methylmagnesium iodide on 4-methoxybenzophenone.

1 : 3-Di-*p*-methoxyphenyl-1 : 3-diphenylbut-1-ene was prepared from the monomer by a method similar to that used for 1 : 1 : 3 : 3-tetraphenylbut-1-ene (see Part I). The product, m. p. 113°, was the same as that obtained by earlier workers.³

1 : 1-Di-*p*-methoxyphenylethylene was prepared by the action of *p*-methoxyphenylmagnesium bromide on *p*-methoxyacetophenone, or of methylmagnesium bromide on di-*p*-methoxybenzophenone. Both reactions gave the olefin directly. The product, after several recrystallizations from benzene and light petroleum, formed pure white plates, m. p. 144—145° (lit.,^{4,5} m. p. 142—144°).

1 : 1 : 3 : 3-Tetra-*p*-methoxyphenylbut-1-ene could not be prepared solid by the method used for the other olefins, but the following method gave a product containing a high percentage of dimer. To a saturated solution of the monomer in benzene sufficient trichloroacetic acid was added to cause a very fast reaction. When this reaction was over, the solution was washed with water to remove acid, evaporated under a high vacuum, and the residue recrystallized from acetic acid. Crystals of monomer were obtained, together with a viscous yellow oil. The molecular weight of this oil, determined by cryoscopic measurements in benzene, was 362. Since the molecular weight of the dimer is 480, we believe that the oil is a monomer-dimer mixture containing 67% of the latter.

1 : 1-Di-*p*-methoxyphenylethane was prepared by a method analogous to that of Anschutz and Hilbert.^{1b} A large (200-fold) excess of sodium was added slowly to a refluxing solution of 1 : 1-di-*p*-methoxyphenylethylene in absolute ethyl alcohol. The warm solution was diluted with water, and the excess of alcohol distilled off. The residual mixture was extracted with ether, and the organic extract recrystallized several times from dry ether and dried light petroleum (b. p. 60—80°). The white powder obtained (60%) had m. p. 71—72°. The latest recorded m. p.³ is 70—72°.

Nitroethane was obtained from Messrs. Light. It was kept over phosphoric oxide for 24 hr., distilled twice under reduced pressure at low temperature, and then fractionated up a 40-cm. point column. The fraction of b. p. 115° was used.

Procedure.—The technique for the dilatometric work was identical with that outlined in Part I. Since the ions produced by addition of protons to these olefins are coloured, the solutions were also examined spectrophotometrically in a Unicam SP 500 spectrophotometer. Master solutions of trichloroacetic acid and olefin were made up independently, known volumes of each pipetted into 10-ml. graduated flasks, and the latter filled to the mark with solvent.

¹ (a) Coops, Heitjink, and Kramer, *Rec. Trav. chim.*, 1953, **72**, 765; (b) Anschutz and Hilbert, *Ber.*, 1924, **57**, 1698.

² Schmitz-Dumont, Thomke, and Diebold, *Ber.*, 1937, **70**, 175.

³ Hurd and Webb, *J. Amer. Chem. Soc.*, 1927, **49**, 549.

⁴ Tarbell and Lindstrom, *ibid.*, 1946, **68**, 1930.

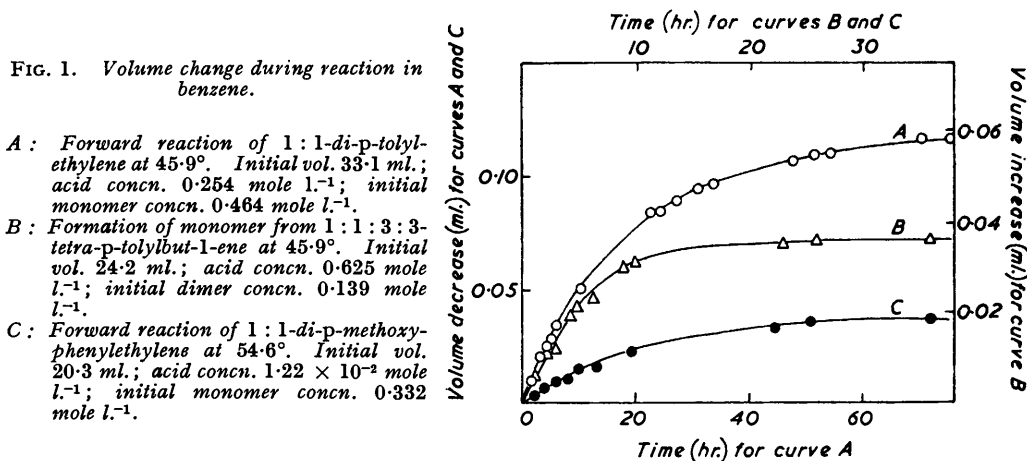
⁵ Price and Mueller, *ibid.*, 1944, **66**, 634.

The spectra of the resulting solutions were observed, 1-cm. silica cells being used. For the system benzene-trichloroacetic acid-1 : 1-di-*p*-methoxyphenylethylene the effect of acid concentration at constant initial monomer concentration, and of monomer concentration at constant initial acid concentration, on the absorption spectrum was examined. The effect of temperature on the absorption was also observed, a photomultiplier technique being used as described earlier.⁶

Results

1 : 1-Di-*p*-tolylethylene.—(a) *Dimerization reaction in benzene.* (i) Analysis of reaction products. The volume change of a solution of trichloroacetic acid and olefin in benzene was followed until no further change was observed. The dilatometer bulbs were then opened, and the acid extracted with water and titrated with alkali. All the acid was recovered unchanged. The non-aqueous layer was evaporated under a high vacuum, and the residual oil washed with acetic acid. A white solid separated which was filtered off, dried, and weighed. It had m. p. 107°, raised by one recrystallization from light petroleum to 108°, and this established the product as 1 : 1 : 3 : 3-tetra-*p*-tolylbut-1-ene.² (Solutions of acid or of olefin alone in benzene showed no volume change during several months.)

By measuring the densities, at different temperatures, of solutions containing pure monomer,



pure dimer, and intermediate mixtures of the same total weight, dissolved in the same volume of benzene, we find that the volume of a given weight of solution varies linearly with the percentage by weight of dimer in it, thus confirming the assumption made in Part I. By this method the volume change occurring when 1 mole of monomer in 1 l. of solution is converted entirely into dimer was found to be 11.78 ml. at 33.8°, 11.90 ml. at 45.9°, and 12.19 ml. at 54.6°. The corresponding values calculated by the method used in Part I, from the volume changes measured in our acid-catalysed reactions, were 11.68 ml., 11.45 ml., and 11.81 ml., respectively. These two sets of values agree with each other within the experimental accuracy.

The reaction does not go to completion, as is shown by the extent of the volume change during reaction. The recovery of dimer from the equilibrium mixture is more difficult in this case than for the dimerization of 1 : 1-diphenylethylene, because the monomer and dimer are both solids of similar solubility in benzene, but the method of recovery outlined above gives a value for the amount of dimer present at equilibrium which is 88% of that predicted by the observed volume change.

(ii) Analysis of reaction curves. A typical reaction curve is shown in Fig. 1. These curves were analysed by the method of initial slopes as in Part I.

(iii) Orders in monomer and acid. The variation of initial rate of reaction (*a*) with acid concentration at constant initial monomer concentration and (*b*) with monomer concentration at constant acid concentration was determined. The results are shown in Figs. 2*a* and 2*b*. The order in monomer is 1.9 ± 0.1 , and in acid 2.8 ± 0.2 at all three temperatures (see Table 3).

(iv) Activation energy of the forward reaction. From the curves shown in Fig. 2 we can calculate the activation energy. A plot of \log_{10} (mean rate constant) against $1/T$ is given in

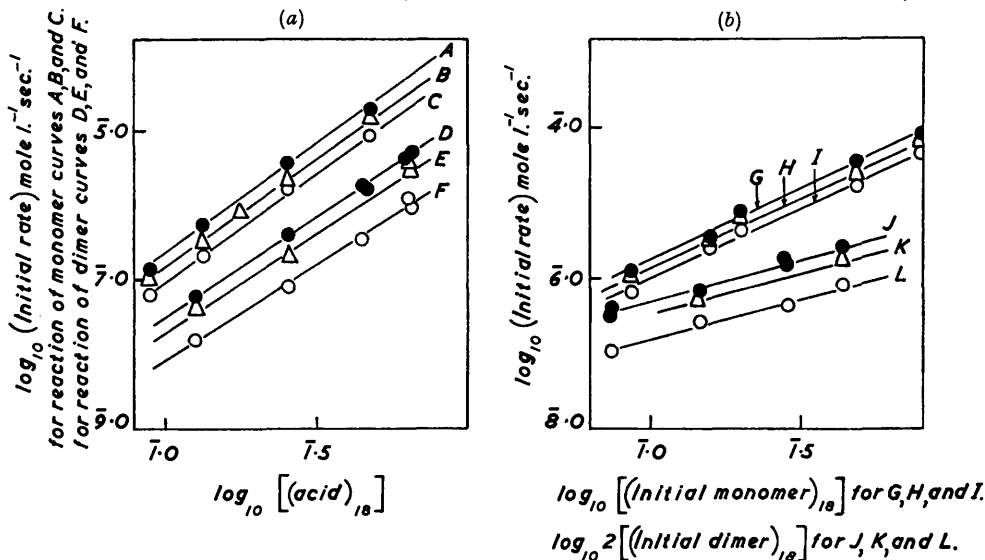
Fig. 3a. The average value of the activation energy is 6.6 ± 0.5 kcal./mole. The rate constants, k_f , were evaluated from the initial rate by using the expression

$$\text{Initial rate of forward reaction} = k_f \times [\text{acid}]^3 \times [\text{initial monomer}]^2$$

where the initial rate is expressed as mole l.⁻¹ of dimer formed per sec. The acid concentration in this expression was calculated by using the molecular weight of the acid dimer (see Part I).

(b) *The reverse reaction.* (i) Analysis of products. This was carried out as in the forward runs. (The benzene solution of dimer in absence of acid gave no change in volume.) The

FIGS. 2a and 2b. Orders in monomer, dimer, and acid in benzene as solvent.
(Monomer = 1 : 1-di-*p*-tolylethylene in benzene. All concentrations in mole l.⁻¹.)



Curve	Temp.	Initial monomer
A	54.6°	0.460
B	45.9	0.463
C	33.8	0.472
		Initial dimer
D	54.6	0.137
E	45.9	0.138
F	33.8	0.140

Curve	Temp.	Acid
G	54.6°	0.252
H	45.9	0.254
I	33.8	0.258
J	54.6	0.434
K	45.9	0.439
L	33.8	0.445

(In order to make Figs. 2a and 2b clearer, we have moved curve A vertically upwards by +0.2, and curves G, H, and I upwards by +1.0.)

dimer recovered from the equilibrium reaction mixture was always about 88% of that expected from the volume change: this volume change was to within 5% the complement of that found when starting from monomer. A typical reaction curve is shown in Fig. 1, and these curves were analysed as for the forward runs.

(ii) Order in dimer and acid. The order plots were made as for the forward runs, and the effect of the concentration of the reactants on the rate is shown in Figs. 2a and 2b. The order in dimer is 1.0 ± 0.2 and that in acid 2.8 ± 0.2 . These orders are independent of temperature.

(iii) Activation energy of the reverse reaction. The rate constants, k_r , were evaluated from the initial rate by using the expression

$$\text{Initial rate of reverse reaction} = k_r \times [\text{acid}]^3 \times [\text{initial dimer}]$$

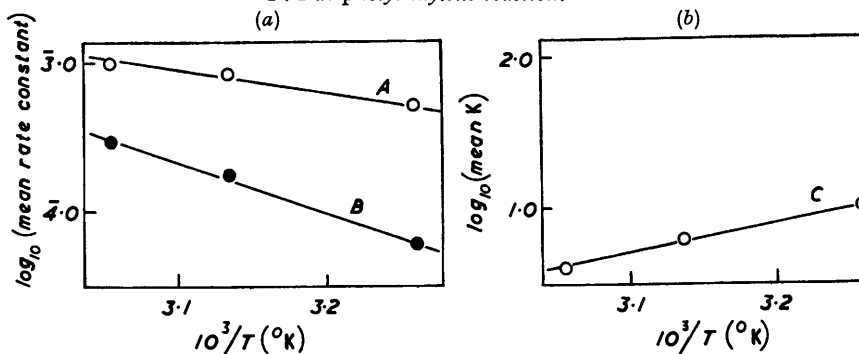
where the initial rate is expressed as mole l.⁻¹ of dimer disappearing per sec., and the acid concentration is expressed in terms of the acid dimer. The activation energy, obtained from \log_{10} (mean rate constant) against $1/T$ plot shown in Fig. 3a, is 14.8 ± 1.5 kcal./mole.

(c) *Determination of the equilibrium constant.* The orders in acid are the same for the forward

and the reverse runs, and so the equilibrium constants have been calculated from the concentrations of monomer and dimer at equilibrium, $[\text{Monomer}]_e$ and $[\text{Dimer}]_e$, by using the expression $K = [\text{Dimer}]_e/[\text{Monomer}]_e^2$ as in Part I, and their values are given in Table 1. The change of \log_{10} (mean K) with $1/T$ is plotted in Fig. 3b. The exothermicity of the reaction ($-\Delta H^\circ$), obtained from the slope of this line, is 8.4 ± 0.5 kcal./mole. A summary of the results is given in Tables 1, 2, and 3.

1-p-Methoxyphenyl-1-phenylethylene.—The dimerization reaction and reverse reaction in benzene. This reaction was similar in all essentials to that described above. No volume change occurred unless both acid and olefin were present. The product was shown² to be the but-1-ene

FIGS. 3a and 3b. Temperature dependence of rate constants and equilibrium constants for the 1:1-di-p-tolylethylene reaction.



A, Dimerization reaction. B, Reverse reaction. C, Dependence of K on T .

dimer by its m. p. 113° , and the acid was completely recovered from the equilibrium reaction mixture. The volume changes when 1 mole of monomer in 1 l. changes completely into dimer, found from the volume change during reaction as described in Part I, are 11.79 ml. at 33.9° , 11.89 ml. at 45.9° , and 12.04 ml. at 54.6° . These results were confirmed by measuring the

TABLE I. Rate constants and equilibrium constants.

Olefin *		Solvent	Temp.	k_t (mole ⁻⁴ l. ⁴ sec. ⁻¹)	k_r (mole ⁻³ l. ³ sec. ⁻¹)	k_t/k_r (mole ⁻¹ l.)	K (mole ⁻¹ l.)
R	R'						
H ^a †	H	C ₆ H ₆	33.8°	1.8×10^{-6}	4.8×10^{-7}	3.8	15.9 ± 0.4
			45.7	3.3×10^{-6}	1.3×10^{-6}	2.5	8.6 ± 0.2
			54.7	4.5×10^{-6}	2.7×10^{-6}	1.7	5.6 ± 0.1
				(mole ⁻⁴ l. ⁴ sec. ⁻¹)	mole ⁻³ l. ³ sec. ⁻¹)		
Me ^b	Me	,,	33.8	4.9×10^{-4}	5.8×10^{-5}	8.5	9.9 ± 0.5
			45.9	8.3×10^{-4}	1.7×10^{-4}	4.8	6.1 ± 0.3
			54.6	9.4×10^{-4}	2.8×10^{-4}	3.4	3.8 ± 0.2
H ^b	MeO	,,	33.7	1.06×10^{-3}	2.2×10^{-4}	4.8	8.5 ± 0.2
			46.0	1.37×10^{-3}	6.1×10^{-4}	2.2	5.7 ± 0.1
			54.6	1.58×10^{-3}	1.1×10^{-3}	1.4	4.7 ± 0.1
				$k_t = k_{1a}$ (mole ⁻³ l. ³ sec. ⁻¹)	—	—	—
MeO ^c	MeO	C ₆ H ₆	33.8	4.9×10^{-1}	—	—	4.6 ± 0.5
			45.9	8.2×10^{-1}	—	—	3.9 ± 0.2
			54.6	1.29×10^0	—	—	3.0 ± 0.2
				$k_t = k_{2a}k_{1a}/k_{1b}$ (mole ⁻³ l. ³ sec. ⁻¹)	$k_r = k_{2b}k_{3b}/k_{3a}$ (mole ⁻² l. ² sec. ⁻¹)		
H ^d	H	NO ₂ Et	34.2	1.9×10^{-6}	3.0×10^{-7}	6.6	13.4 ± 0.5
			45.8	3.0×10^{-6}	7.1×10^{-7}	4.2	7.3 ± 0.4
			54.6	3.9×10^{-6}	1.37×10^{-6}	2.8	5.0 ± 0.2

Initial rate constants are given in moles of dimer formed or lost per l. per sec. for unit concentration of reagents in mole l.⁻¹.

^a Order in acid 3.1, in monomer 2, in dimer 1 (from Part I). ^b Order in acid 3, in monomer 2, in dimer 1. ^c Order in acid 3, in monomer 1. ^d Order in acid 2.4, in monomer 2.

* In Tables 1, 2, and 3, R and R' relate to the olefin *p*-C₆H₄R·C(CH₃)₂·C₆H₄R'·*p*.

† From Part I (*loc. cit.*).

TABLE 2. Changes in energy and entropy.

Olefin		Solvent	E_t	E_r	$-(E_t - E_r)$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
R	R'		(kcal. mole ⁻¹)	(kcal. mole ⁻¹)	(kcal. mole ⁻¹)	(kcal. mole ⁻¹)	(kcal. mole ⁻¹)	(cal. mole ⁻¹ deg. ⁻¹)
			$E_t = (\Delta H^\circ_1 + E_{2a})$	$E_r = (-\Delta H^\circ_3 + E_{2b})$			$34^\circ \pm 0.2^\circ$	$34^\circ \pm 0.2^\circ$
			$RT \ln K$					
H*	H	C ₆ H ₆	9.1 ± 0.5	17.3 ± 1.5	8.2 ± 2.0	10.1 ± 0.5	1.69	27.4
Me	Me	"	6.6 ± 0.5	14.8 ± 1.5	8.2 ± 2.0	8.4 ± 0.5	1.41	22.8
H	MeO	"	5.2 ± 0.5	14.6 ± 1.5	9.4 ± 2.0	6.0 ± 0.5	1.32	15.3
MeO	MeO	C ₆ H ₆	$E_t = E_{1a}$ 9.4 ± 0.5	—	—	3.3 ± 0.5	0.93	7.8
H	H	NO ₂ Et	$E_t = (\Delta H^\circ_1 + E_{2a})$ 6.8 ± 0.5	$E_r = (-\Delta H^\circ_3 + E_{2b})$ 14.3 ± 1.5	7.5 ± 2.0	9.7 ± 0.5	1.59	26.4

ΔH° , ΔG° , and ΔS° are for the 1 mole l.⁻¹ standard state.

* From Part I (*loc. cit.*).

TABLE 3. Order in reactants.

Olefin		Solvent	Orders in acid :		Order in monomer	Order in dimer
R	R'		forward runs	reverse runs		
H*	H	C ₆ H ₆	3.1 ± 0.2	3.1 ± 0.2	2.0 ± 0.1	1.0 ± 0.2
Me	Me	"	2.8 ± 0.2	2.8 ± 0.2	1.9 ± 0.1	1.0 ± 0.2
H	MeO	"	3.1 ± 0.2	3.1 ± 0.2	2.0 ± 0.1	1.0 ± 0.2
MeO	MeO	C ₆ H ₆	2.8 ± 0.2	—	1.0 ± 0.1	—
H	H	NO ₂ Et	2.4 ± 0.2	2.4 ± 0.2	2.1 ± 0.1	1.2 ± 0.2

* From Part I (*loc. cit.*).

densities at different temperatures for solutions of dimer and monomer as described in Part I. Again, only 88% of the yield of dimer expected from the volume change could be recovered from the equilibrium solution. The orders in reactants and the activation energies for the forward and reverse reactions, and the equilibrium constants and the exothermicity ($-\Delta H^\circ$) of the overall reaction were determined as for the previous cases, and the results are given in Tables 1—3.

1 : 1-Di-*p*-methoxyphenylethylene.—*The dimerization reaction in benzene.* (i) Analysis of products. The product has been isolated only as an oil, but this has been shown cryoscopically to be at least 67% dimer. This is supported by the fact that a solution of the oil in a benzene-trichloroacetic acid mixture undergoes an appreciable volume increase with time. Since we have not isolated the pure dimer we cannot determine the volume change for the complete conversion of monomer into dimer in this case. The corresponding volume changes for the three previously discussed monomers, however, have agreed to within 4%, as one might expect since the *para*-substituents should have little effect on the volume change for the complete conversion of monomer into dimer. Thus we have assumed that the volume change when 1 mole of 1 : 1-di-*p*-methoxyphenylethylene in 1 l. goes completely into dimer is the same as that for 1 : 1-diphenylethylene. Experimental justification for this will be given later.

On this basis we have estimated the weight of unchanged monomer in solution at equilibrium from the observed volume change. Analysis of the products as before gave complete acid recovery, and after treatment in a high vacuum an ethereal solution of the residue deposited an amount of monomer (m. p. 144°) which was 95% of that estimated as above.

(ii) *Orders in acid and monomer.* The reaction curve (see Fig. 1) was analysed by the method of initial slopes, and the orders were found as described above (see Figs. 4a and 4b). The order in acid is 2.8 ± 0.2 , and that in monomer is 1.0 ± 0.1 (see Table 3). The latter value is in strong contrast with the monomer order of 2 obtained for the monomers discussed above.

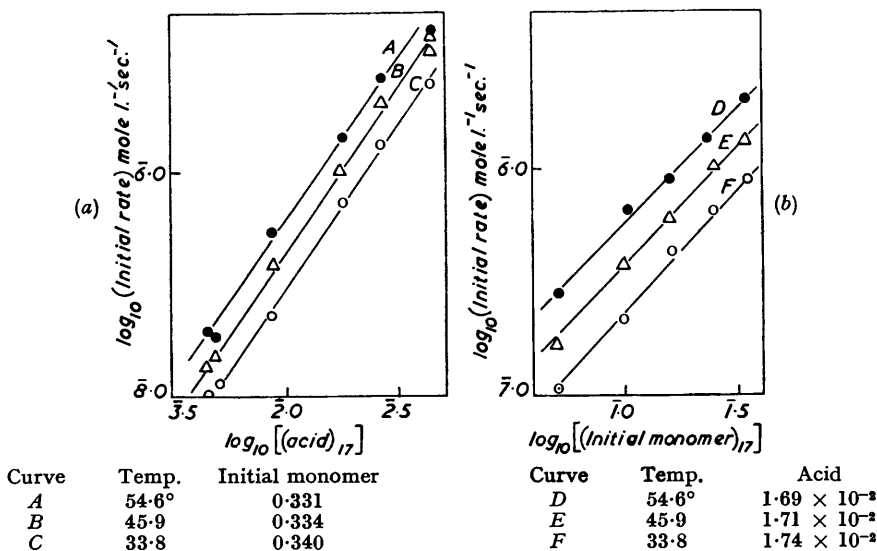
(iii) *Activation energy.* The rate constant, k_t , was evaluated from the initial rate by using the expression

$$\text{Initial rate of forward reaction} = k_t \times [\text{acid}]^3 \times [\text{initial monomer}]$$

the same units being used for initial rate and acid concentration as for the other olefins. From the dependence of k_t on temperature (see Fig. 5a) the activation energy, E_t was found to be 9.4 ± 0.5 kcal./mole.

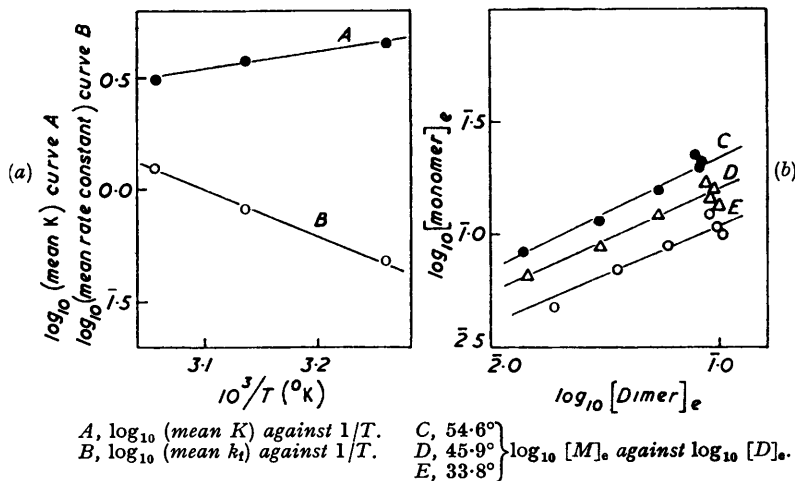
(iv) Equilibrium constant. Assuming that the volume change for the conversion of 1 mole of monomer completely into the dimer is the same in this case as for 1:1-diphenylethylene, we have estimated the concentrations of monomer and dimer at equilibrium, $[\text{Monomer}]_e$ and $[\text{Dimer}]_e$, in the 1:1-di-*p*-methoxyphenylethylene reactions from the observed volume change.

FIGS. 4a and 4b. Orders in monomer and acid for 1:1-di-*p*-methoxyphenylethylene. (Concentrations in mole l.⁻¹.)



(In order to make Fig. 4a clearer, we have moved curves B and C vertically downwards by +0.1 and +0.2, respectively.)

FIGS. 5a and 5b. Rate constants and equilibrium constants for 1:1-di-*p*-methoxyphenylethylene.



(Curve C has been raised vertically by 0.1, and curve E lowered by 0.1.)

If we plot $\log_{10} [\text{Monomer}]_e$ against $\log_{10} [\text{Dimer}]_e$ at equilibrium (see Fig. 5b) we obtain a straight line of slope 0.5 (as we do for the other olefins), which is the value one should get for a dimerization of this type having an equilibrium constant $K = [\text{Dimer}]_e / [\text{Monomer}]_e^2$. The fact that the lines are straight, and of slope 0.5, is strong support for the assumption we have had to make in this case about the overall volume change. The mean values of K are given in Table 1. From the K values at the three temperatures, the exothermicity ($-\Delta H^\circ$) has been found to be 3.3 ± 0.5 kcal./mole (see Fig. 5a).

We have not been able to isolate the pure dimer and so have not carried out the reverse runs for this olefin.

1 : 1-Diphenylethylene.—The dimerization and the reverse reactions in nitroethane. (i) Analysis of products. The product of the forward reaction has been established as 1 : 1 : 3 : 3-tetra-phenylbut-1-ene in the same way as for the benzene solution (Part I). The dimerization

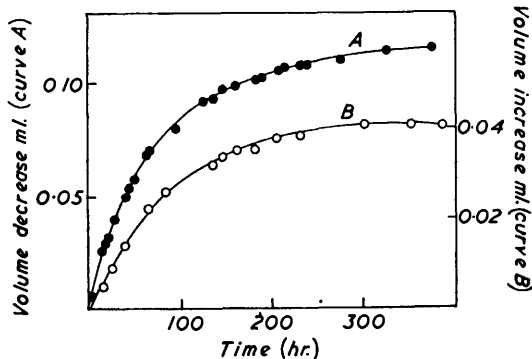
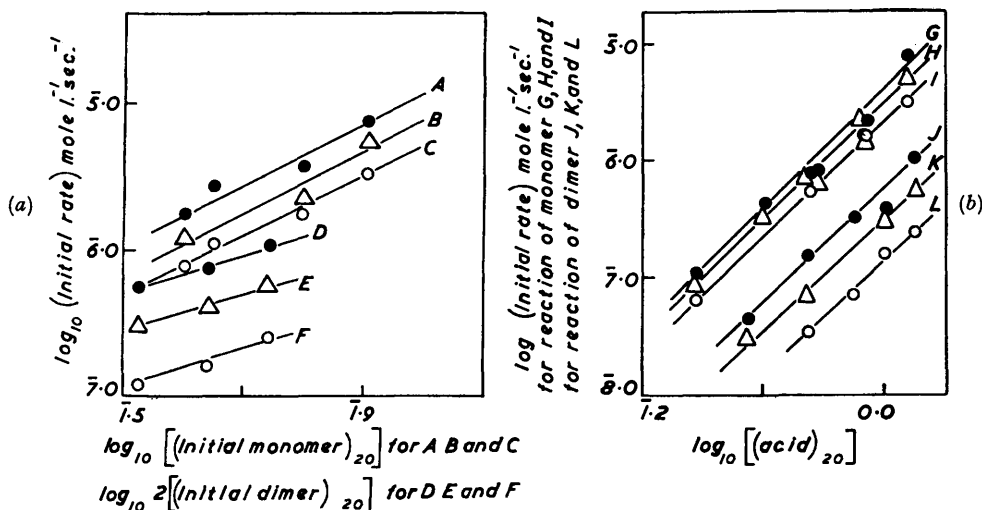


FIG. 6. Volume change during reaction in nitroethane.

A : Forward reaction of 1 : 1-diphenylethylene at 45.8°. Initial vol. = 16.1 ml.; acid concn. = 0.858 mole l.⁻¹; initial monomer concn. = 0.799 mole l.⁻¹.

B : Formation of monomer from 1 : 1 : 3 : 3-tetra-phenylbut-1-ene at 45.8°. Initial vol. = 27.0 ml.; acid concn. = 1.15 mole l.⁻¹; initial dimer concn. = 0.278 mole l.⁻¹.

FIGS. 7a and 7b. Orders in monomer, dimer, and acid in nitroethane as solvent. (Monomer = 1 : 1-diphenylethylene in nitroethane. Concentrations in mole l.⁻¹.)



Curve	Temp.	Acid	Curve	Temp.	Initial monomer
A	54.6°	1.213	G	54.6°	0.768
B	45.8	1.225	H	45.8	0.776
C	33.8	1.242	I	33.8	0.786
D	54.6	1.213			Initial dimer
E	45.8	1.225	J	54.6	0.267
F	33.8	1.242	K	45.8	0.270
			L	33.8	0.273

proceeds only in the presence of both olefin and acid; no volume change occurs when olefin and solvent or when acid and solvent are kept together for several weeks. Neither the forward nor the reverse reaction, however, attains a steady equilibrium volume. There is some side reaction involving a volume decrease which causes a continuous drift of volume after all the dimerization, or all the reverse reaction, should be complete. This effect, which is slight at 34.2° and only becomes appreciable at 54.7°, is an interaction requiring the presence of all three components of the system (see Fig. 6). It was possible, however, to estimate the volume change which would have resulted if no drift had occurred, and to use these values, as described in Part I, to calculate the volume change for the complete conversion of 1 mole of monomer into dimer in

1 l. of solution. The values so obtained are 10.29 ml. at 34.2°, 10.25 ml. at 45.8°, and 10.43 ml. at 54.7°. These values agree within 4% with the values found from density measurements. Complete recovery of acid was obtained, and the weights of dimer regained from the equilibrium solutions agreed, to within 5%, with the values calculated from the reaction volume change.

(ii) Orders in reactants. By the method of initial slopes the order in monomer is 2.1 ± 0.1 , and in dimer is 1.2 ± 0.2 (see Table 3 and Fig. 7a). The order in acid for both the forward and the reverse runs is 2.4 ± 0.2 at all three temperatures (see Fig. 7b) and these are seen to be lower than the values obtained in benzene as solvent.

(iii) Activation energies. The rate constants k_f and k_r have been calculated by using the following expressions:

$$\text{Initial rate of forward reaction} = k_f \times [\text{acid}]^{2.4} \times [\text{initial monomer}]^2$$

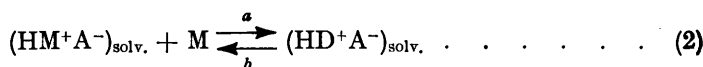
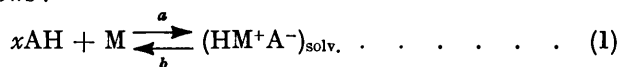
$$\text{Initial rate of reverse reaction} = k_r \times [\text{acid}]^{2.4} \times [\text{initial dimer}]$$

the same units as above being used for initial rate and acid concentration. The activation energies E_f and E_r have been obtained from the temperature dependence of k_f and k_r , and their values are given in Table 2. They are seen to be lower than those obtained for this olefin in benzene.

(iv) Equilibrium constants. The equilibrium constants have been calculated, as in Part I, from the volume changes occurring in reaction. They are given in Table 1, together with the rate constants.

DISCUSSION

(i) *General Mechanism.*—The results for all the olefins studied show that the reaction mechanism can be written as follows:



where M is monomer, D is dimer, AH is acid, and the solvation of the ion pair includes $(x - 1)$ molecules of AH.

(ii) *1-p-Methoxyphenyl-1-phenylethylene and 1:1-Di-p-tolyethylene in Benzene.*—For these two olefins the orders in acid, monomer, and dimer are 3, 2, and 1, respectively, and the solutions of olefin-acid-benzene are coloured from the beginning of the reaction. Thus they fall into the same class as 1:1-diphenylethylene in benzene (see Part I), that is, x is 3, and the rate-controlling steps for the forward and the reverse reactions are (2a) and (2b) respectively. Thus $k_f = k_{2a}K_1 = k_{2a}k_{1a}/k_{1b}$, and $k_r = k_{2b}/K_3 = k_{2b}k_{3b}/k_{3a}$.

The high order in acid we attribute to the fact that one acid molecule donates a proton to the olefin, and two acid molecules are included in the solvation of the ion pair.

High orders in acid have also been observed in other acid-catalysed reactions. In the addition of hydrogen chloride to *isobutene*⁷ and of hydrogen bromide to propene,⁸ orders in acid of about 3 have been observed. The cleavage of diethyl ether by hydrogen bromide in a variety of solvents⁹ has given an acid order of 2 in toluene and chlorobenzene, 1.5 in chloroform, and 1 in acetic acid. In the depolymerization of paraldehyde¹⁰ by mono-, di-, and tri-chloroacetic acid, and by hydrogen chloride in several solvents, the order in acid varied with temperature and acid strength but was generally about 2.

In Part I we found a four-fold discrepancy between the ratio of k_f/k_r and K , owing, we suggested, to an impurity in the dimer, which resulted in an increased rate of the reverse reaction. In the case of the 1-*p*-methoxyphenyl-1-phenylethylene, the results (Table 1)

⁶ Bentley, A. G. Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711; Bentley and A. G. Evans, *J.*, 1952, 3468.

⁷ Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339.

⁸ Mayo and Savoy, *ibid.*, p. 1349.

⁹ Mayo, Hardy, and Schultz, *ibid.*, 1941, **63**, 427.

¹⁰ Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1792.

again show a discrepancy between k_t/k_r and K of about two- to three-fold. Here again we believe the values of k_t and K to be the more accurate and the value of k_r obtained from these two quantities to be a better value than that found from the initial slopes of the reverse reaction.

In the case of 1 : 1-di-*p*-tolylethylene, the values of k_t/k_r and K agree to within 20%. This excellent agreement we believe is due to the fact that in this case a method of purification of the dimer was adopted which was more rigorous than in the previous cases, and this result supports our view that it is the results for the initial rates of the reverse reaction which are the least reliable in the earlier cases. Further evidence on this point is given by the fact that values of k_r obtained from the dimer of 1 : 1-di-*p*-tolylethylene purified by the old technique give values of k_t/k_r which are half that of the corresponding K value.

(iii) 1 : 1-Diphenylethylene in Nitroethane.—The results for this system show that the mechanism is identical with that for this monomer in benzene, with the slow forward and reverse steps as reactions 2*a* and 2*b*, respectively, but with the important difference that the order in acid in both forward and reverse reactions is 2·4 instead of 3. This we attribute to the fact that nitroethane is a much better solvent for ions than is benzene (see Part I), and so the solvation of the ion-pairs does not involve trichloroacetic acid molecules to such a high degree.

(iv) 1 : 1-Di-*p*-methoxyphenylethylene in Benzene.—As yet, we have been able to follow only the forward reaction in quantitative detail in this case. For this, the order in acid is 3, but, in strong contrast to the previous olefins we have examined, the order in monomer is unity. Thus we have the rate expression

$$\text{Initial rate of forward reaction} = k_t \times [\text{acid}]^3 \times [\text{initial monomer}]$$

We interpret these results on the same system of reactions as given previously (equations 1, 2, and 3), but we consider the slow forward step to be reaction (1*a*). This would give the expression

$$\text{Initial rate of forward reaction} = k_{1a}[\text{AH}]^3[\text{M}]$$

which is of the same form as that found experimentally where $k_t = k_{1a}$. This interpretation is supported by the fact that, even at high acid concentrations where the ionic concentrations will be the most easily detectable colorimetrically, the solution is colourless during the early stages of the forward reaction, whereas when equilibrium has been established it is coloured. For all the other olefins we have so far studied, the olefin-acid-solvent system is coloured throughout the whole of the reaction and at equilibrium.

The value of K for the overall reaction is given by the expression $K = [\text{Dimer}]_e / [\text{Monomer}]_e^2$ and is related to the individual velocity constants as follows :

$$K = \frac{k_{1c}}{k_{1b}} \cdot \frac{k_{2a}}{k_{2b}} \cdot \frac{k_{3a}}{k_{3b}} = K_1 K_2 K_3$$

For this olefin, $k_t = k_{1a}$ and so k_r is not equal to K/k_t and a knowledge of K cannot be used to find k_r from the value of k_t .

(v) *Ionic Concentrations*.—Since the ionic intermediates which we postulate should have a characteristic absorption spectrum, it would be good evidence for the proposed mechanism if we could show spectroscopically that the equilibrium concentrations of such ions were dependent on the acid and olefin concentration in the way demanded by equations (1), (2), and (3). We have been able to show this to be so for equation (1) in the case of 1 : 1-di-*p*-methoxyphenylethylene. For this olefin the spectrum of the equilibrium mixture of monomer and dimer in a benzene solution of high trichloroacetic acid concentration is very similar in shape (for several hours) to that of the monomer in concentrated sulphuric acid (see Fig. 8), in which latter solution (by analogy with the case of 1 : 1-diphenylethylene in the same acid^{11, 12, 13}) we should expect the monomer ion to be present. Further, in the solutions used for this spectroscopic examination the olefin concentration

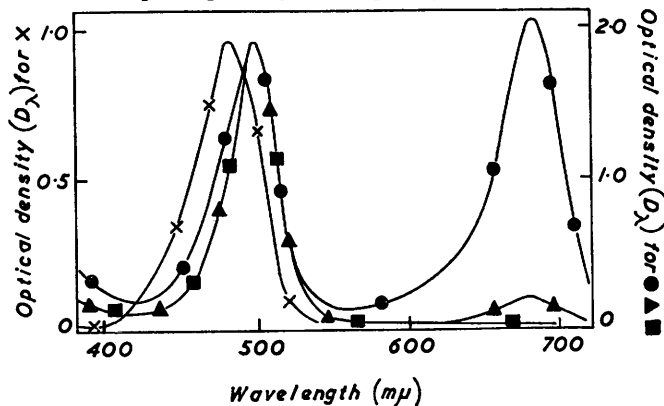
¹¹ A. G. Evans and Hamann, *Proc. Roy. Dublin Soc.*, 1950, 25, 1939; A. G. Evans, *J. Appl. Chem.*, 1951, 1, 240.

¹² Gold and Tye, *J.*, 1952, 2172.

¹³ Gold, Hawes, and Tye, *ibid.*, p. 2167.

has to be very small, and under the conditions we have used, about 80–95% of the olefin will be present as monomer (as calculated from K), after the very rapid attainment of equilibrium. Thus we have taken the value of $\int D_\lambda \cdot d\lambda$ of the spectrum as a measure of the concentration of the monomer ions in these equilibrium solutions, since the spectrum is so similar to that of the olefin in concentrated sulphuric acid and since the concentration

FIG. 8. Absorption spectra of 1 : 1-di-*p*-anisylethylene solutions at 20°.



A : 1.73×10^{-5} mole l^{-1} of olefin in 98% H_2SO_4 .

B, C, and D : 6.7×10^{-4} mole l^{-1} of olefin and 1.18 mole l^{-1} of trichloroacetic acid in benzene solution.

× Curve A

■ Curve B after 20 min.

▲ Curve C after 5 hr.

● Curve D after 143 hr. (after this time, no further change in the spectrum occurred).

(The symbols on these curves do not represent the experimental points, but are used to characterise the different curves.)

FIGS. 9a and 9b. Dependence of the optical density on acid and olefin concentrations in the 1 : 1-di-*p*-methoxyphenylethylene–benzene–trichloroacetic acid system at equilibrium.

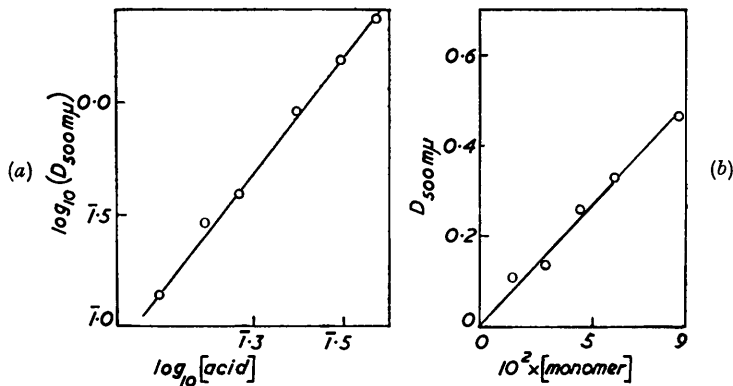


FIG. 9a. Constant total olefin concn. expressed as monomer = 2.96×10^{-2} mole l^{-1} . (Temp. 18.0°.)

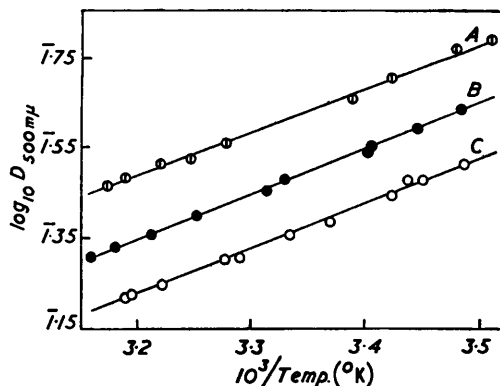
FIG. 9b. Constant acid concn. = 1.23×10^{-1} mole l^{-1} . (Temp. 18.0°.)

of dimer ions will be so much smaller than those of the monomer ions. Making these assumptions, we have found the effect of acid concentration and total 1 : 1-di-*p*-methoxyphenylethylene concentration on the monomer ion concentration of the olefin–acid–benzene solutions which have attained equilibrium. The results are shown in Fig. 9 (D_λ is proportional to $\int D_\lambda \cdot d\lambda$) for the case where (a) acid is varied at constant total olefin concentration, and (b) olefin is varied at constant acid concentration. It is found that the concentration

of the monomer ions (taken as proportional to D_{500}) depends on the acid concentration to the power 2.7 ± 0.2 and on total olefin concentration to the power 1.0. This is conclusive evidence that equilibrium (1) exists. In Fig. 10 we give typical plots of $\log_{10} D_{500}$ against $1/T$. From the slopes of these lines, allowing for the normal expansion of the solution, we obtain a value of $+3.5 \pm 0.2$ kcal./mole for the exothermicity ($-\Delta H^\circ_{1a}$) of reaction (1a) in this system.

We may obtain an approximate value for the concentration of monomer ions in this system by making the further assumption that, although there is a peak shift of 13 $m\mu$ (see Fig. 8), the value of $\int D_\lambda \cdot d\lambda$ is the same in these solutions as for the same concentration of R^+ ions in concentrated sulphuric acid. This method of determining the R^+ ion concentration has been justified by experiments made on solutions of tri-*p*-tolylmethyl halides in *m*-cresol, where a peak shift of 4 $m\mu$ was obtained.¹⁴ In this way we find that for a total olefin concentration of 6.4×10^{-3} mole l^{-1} (measured in terms of monomer) and acid concentration of 4.4×10^{-1} mole l^{-1} (measured in terms of the dimer acid), the

FIG. 10. *Effect of temperature on the colour of the 1 : 1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system at equilibrium.*



Curve	Acid concn. (mole l^{-1})	Total olefin concn. expressed as monomer (mole l^{-1})
A	2.46×10^{-1}	1.94×10^{-2}
B	3.06×10^{-1}	6.36×10^{-3}
C	2.30×10^{-1}	6.36×10^{-3}

concentration of monomer ions is 1.7×10^{-5} g.-ion l^{-1} . Thus $K_1 = 3.1 \times 10^{-2}$ mole $^{-3}l^3$, and $\Delta S^\circ_{1a} = -19$ cal. deg. $^{-1}$ mole $^{-1}$ for the 1 : 1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system at 18°.

(vi) *Acid-Olefin Interaction.*—When the trichloroacetic acid-benzene solutions of 1 : 1-di-*p*-methoxyphenylethylene which gave the spectrum *B*, shown in Fig. 8, are left for long periods it is found that a second peak develops at *ca.* 680 $m\mu$ (see Fig. 8, curves *C* and *D*). This second peak does not develop at all in concentrated sulphuric acid solutions of this olefin. For the concentrations of the experiment shown in Fig. 8, the peak at 500 $m\mu$ (curve *B*) develops immediately and remains virtually unchanged with time. This phenomenon must mean that, when this olefin is dissolved in trichloroacetic acid-benzene mixtures, there is (a) a rapid proton transfer to form the classical carbonium ion $^+CR_2Me$ similar to that existing in the concentrated sulphuric acid solutions of the olefin (by analogy with the case of 1 : 1-diphenylethylene in this acid^{11, 12, 13}), and (b) a slow interaction of the olefin with the acid to give a coloured species different from this classical carbonium ion. During the time taken to achieve the monomer-dimer equilibrium in our dilatometric experiments, this second species is present in negligible concentration, and so we consider that the effective ion intermediate in the dimerization (equations 1, 2, and 3) is the classical ion.

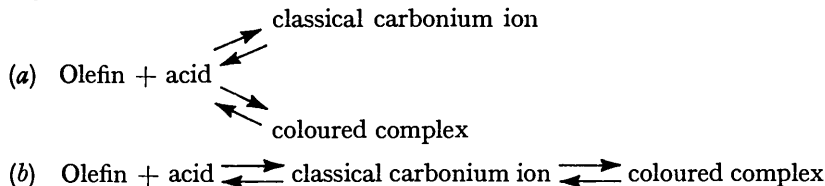
¹⁴ A. G. Evans, McEwan, Price, and Thomas, *J.*, 1955, 3098.

It is of great importance, however, to investigate further the nature of the second coloured species. This species might be due to the interaction of the acid (*a*) with the olefin double bond, or (*b*) with some part of the olefin molecule other than the double bond. To determine which of these alternatives is correct, we have examined a solution of 1 : 1-di-*p*-methoxyphenylethane in benzene-trichloroacetic acid. (Concentrations : 1 : 1-di-*p*-methoxyphenylethane 3.1×10^{-3} mole l.⁻¹, trichloroacetic acid 1.35 mole l.⁻¹.) This solution was colourless even after 700 hr. Since the concentrations here are greater than those for the olefin experiment shown in Fig. 8, it is clear that the peak in the 680 m μ region must be due to a coloured species formed by the interaction of the acid with the olefin double bond. For a solution of olefin and acid of comparable concentration to this ethane-acid system the optical density of the 680 m μ peak would be 10.5.

Taft, Purlee, Reitz, and DeFazio¹⁵ have recently suggested that two distinct species may be formed by the interaction between acid and olefin to account for their results on olefin hydration. They suggest a rapid equilibrium formation of a π -complex followed by the slow rate-determining isomerization of this to the classical ion, and the subsequent reaction of this classical carbonium ion with water to give the alcohol.

Our work, therefore, supports these authors' suggestion that two distinct species may be formed, and can coexist, in the interaction of an acid with an olefin, *viz.*, (*a*) a classical carbonium ion $^+CR_2Me$ in which the proton donated by the acid forms a covalent bond with the carbon atom, and (*b*) a complex which may be written $\begin{matrix} R \\ \diagdown \\ C \\ \diagup \\ R \end{matrix} \begin{matrix} H^+ \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{matrix} CH_2$ in which the proton from the acid is associated in some way with the olefin double bond. The fact that under the conditions of our experiments both these species have an independent existence is conclusively demonstrated by their entirely different rates of formation. [Since the species can coexist, the migration of the proton from the double bond to the 2-carbon atom, or *vice versa*, either directly or through the (olefin + acid) initial state, must involve the surmounting of a free-energy barrier.]

Our present results, however, do not show that the complex is formed first and that the classical ion is subsequently produced from it, but indicate either or both of the following mechanisms :



Further work is being carried out on these coloured species in various olefin-acid systems, since preliminary experiments have shown that many such systems have two absorption peaks in the visible region.

The measurements of classical carbonium-ion concentrations, described in section (v) and shown in Figs. 9 and 10, were carried out on solutions which had reached monomer-dimer equilibrium, but had not had time to develop any peak due to this coloured complex.

(vii) *Effect of Substituents.*—(a) *When the rate-determining step is reaction (2a).* As the power of the *para*-substituent group to promote ionization increases, two effects are observed. First, the overall equilibrium constant $K (= K_1K_2K_3)$ decreases; this means that the introduction of such a *para*-substituent group reduces the free energy of the initial state of the overall reaction (*i.e.*, two solvated monomer molecules) with respect to the final state of the overall reaction (*i.e.*, one solvated dimer molecule). Secondly, the velocity constant of the forward reaction $k_f (= k_{2a}k_{1a}/k_{1b})$ increases; so the reduction in free energy of the transition state of reaction (2a) with respect to the final state of the overall reaction is greater than is the corresponding reduction for the initial state of the overall reaction.

¹⁵ Taft, Purlee, Reitz, and DeFazio, *J. Amer. Chem. Soc.*, 1955, **77**, 1587.

The energy values found for these reactions show that the introduction of these *para*-substituents causes ΔH° ($= \Delta H^\circ_{1a} + \Delta H^\circ_{2a} + \Delta H^\circ_{3a}$) to become more positive, and E_t ($= \Delta H^\circ_1 + E_{2a}$) to become less positive. Thus the effect of these groups on the energies of these states follows their effect on the corresponding free energies.

Further, we find that the temperature-independent factor, A , of the rate equation, $k_t = A \exp(E_t/RT)$, is virtually unaffected by the introduction of these *para*-substituents [*i.e.*, ΔS_t^\ddagger ($= \Delta S^\circ_1 + \Delta S_{2a}^\ddagger$) is practically constant], and so the effect of these groups on the rate constants, k_t , is due almost entirely to their effect on the energies of the states involved. This is to be expected since these substituent groups are in the *para*-position and so will not effect the solvation of the transition state. ΔS_t^\ddagger is very negative for these three olefins (-58.0 , -57.0 , -58.0 cal. mole⁻¹ deg.⁻¹ for the 1 mole l.⁻¹ standard state for the unsubstituted, the di-*p*-methyl-substituted and the mono-*p*-methoxy-substituted 1 : 1-diphenylethylenes, respectively). We attribute this to the fact that there are so many molecules having special orientation in the transition state of reaction 2*a*.

In contrast to the above it is seen that as ΔH° becomes more positive with introduction of the *para*-substituents, ΔS° ($= \Delta S^\circ_{1a} + \Delta S^\circ_{2a} + \Delta S^\circ_{3a}$) also becomes more positive.

(*b*) *When the rate-determining step is reaction (1a).* For the case of 1 : 1-di-*p*-methoxyphenylethylene the values of ΔH° and of ΔS° fall into line with the other olefins studied. This is to be expected since these values are not dependent on mechanism. The value of k_t ($= k_{1a}$) is high, but we cannot compare it directly with the other k_t values because of the difference in mechanism. The activation energy E_t ($= E_{1a}$) is 9.4 kcal./mole. The entropy of activation ΔS_t^\ddagger ($= \Delta S_{1a}^\ddagger$) is -31.8 cal. deg.⁻¹ mole⁻¹, which is more positive than are those for the other olefins studied, owing, we believe, to the fact that only one monomer is involved in the transition state of the rate-determining step, reaction (1*a*). The fact that the entropy of activation is more favourable for this mechanism than for that in which reaction (2*a*) is the slow step, means that the change of the rate-determining step from (2*a*) to (1*a*) will occur even before the value of E_{1a} is less than that of ($\Delta H^\circ_{1a} + E_{2a}$).

A fuller discussion of the effect of substituents will be given later.

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